Unclassified
SECURITY CLASSIFICATION OF THIS PAGE

(4)

AD-A208 273

REPORT DC

DTIC ELECTE JUN 0 1 1989 S D

FILE COPY

1a. REPORT SECURITY CLASSIFICATION: Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT: Approved for public release distribution unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. NAME OF PERFORMING ORGANIZATION: Rensselaer Polytechnic Institute; 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION: ONR
6c. ADDRESS (City, State, and ZIP Code): Department of Chemistry, Troy, New York 12180-3590	7b. ADDRESS (City, State, and ZIP Code): Department of Navy, Arlington, Virginia 22217
8a. NAME OF FUNDING/SPONSORING ORGANIZATION: ONR; 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: Contract # N00014-85-K-0632
8c. ADDRESS (City, State, and ZIP Code): Department of Navy, Arlington, Virginia 22217	10. SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification): Chemical Vapor Deposition of Silicon Carbide Using a Novel Organometallic Precursor

12. PERSONAL AUTHOR(S): Leonard V. Interrante, Corinna L. Czekaj, John Hudson, Klaus Lenz, and Bing-Xi Sun, Wei Lee

13a. TYPE OF REPORT	13b. TIME COVERED FROM ____ TO ____	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Publication			7

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	CVD, silicon carbide, organometallic precursor; (KT)

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Dense silicon carbide films have been prepared by low pressure chemical vapor deposition (LPCVD) using a volatile, heterocyclic, carbosilane precursor, $MeHSiCH_2SiCH_2Me(CH_2SiMeH_2)$. At deposition temperatures between 700 and 800°C, polycrystalline, stoichiometric SiC films have been deposited on single crystal silicon and fused silica substrates. Optical microscopy and SEM analyses indicated formation of a transparent yellow film with a uniform, featureless surface and good adherence to the Si(111) substrate. The results of preliminary studies of the nature of the gaseous by-products of the CVD processes and ultrahigh vacuum physisorption and decomposition of the precursor on Si(100) substrates are discussed.

Keywords: organic chemistry; physical chemistry; silica; films;

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL: David Nelson	22b. TELEPHONE (Include Area Code): (202) 696-4409 / 22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

OFFICE OF NAVAL RESEARCH

Contract N00014-85-K-0632

Task No. 625-826

Technical Report No. 5

Chemical Vapor Deposition of Silicon Carbide Using a Novel Organometallic Precursor

by

Wei Lee, Leonard V. Interrante, Corrina Czekaj, John Hudson, Klaus Lenz, and Bing-Xi Sun

Prepared for Publication

in the

MRS Symposium Proceedings

Rensselaer Polytechnic Institute
Department of Chemistry
Troy, New York 12180

May 15, 1989

CHEMICAL VAPOR DEPOSITION OF SILICON CARBIDE USING A NOVEL ORGANOMETALLIC PRECURSOR

WEI LEE*, LEONARD V. INTERRANTE*, CORRINA CZEKAJ*, JOHN HUDSON**, KLAUS LENZ** AND BING-XI SUN**

*Departments of Chemistry and **Materials Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180-3590.

ABSTRACT

Dense silicon carbide films have been prepared by low pressure chemical vapor deposition (LPCVD) using a volatile, heterocyclic, carbosilane precursor, $MeHSiCH_2SiCH_2Me(CH_2SiMeH_2)$. At deposition temperatures between 700 and 800°C, polycrystalline, stoichiometric SiC films have been deposited on single crystal silicon and fused silica substrates. Optical microscopy and SEM analyses indicated formation of a transparent yellow film with a uniform, featureless surface and good adherence to the Si(111) substrate. The results of preliminary studies of the nature of the gaseous by-products of the CVD processes and ultrahigh vacuum physisorption and decomposition of the precursor on Si(100) substrates are discussed.

INTRODUCTION

The chemical vapor deposition (CVD) of silicon carbide has a long history of development and successful application [1]. However, the full potential of this material, and the CVD method for its generation, has not been realized, in part due to the extreme temperatures (>1000°C) and exacting conditions required by the existing approaches. In particular, its large band gap, high-temperature stability, high thermal conductivity, high breakdown electric field, and high electron saturation velocity make it an attractive candidate for use as a high temperature, radiation-resistant semiconductor [2-5]. Similarily, its hardness, oxidation and corrosion resistance suggest a wide range of potential applications for protective, abrasion and corrosion resistant coatings. One of the problems associated with the use of SiC for such applications is the fact that it can exist in a variety of crystalline modifications and is difficult to obtain as a single-phase material in high compositional purity. Another major problem is the high temperature which is generally required to obtain high-quality SiC by the existing CVD methods.

Silicon carbide thin films of widely varying composition and morphology have been prepared by a range of chemical vapor deposition techniques [1]. These are usually based on the pyrolysis of mixtures of silicon and carbon containing compounds, such as $SiCl_4$ with CCl_4, $HSiCl_3$ with C_6H_{14}, or SiH_4 with C_3H_8. Single-component SiC precursors, such as CH_3SiCl_3, have also been employed. These processes are generally carried out at atmospheric pressure. A carrier gas, such as H_2, He, Ar, or N_2 is generally used, with H_2 often needed for the complete removal of chlorine as HCl. Deposition temperatures range from 800 to 1800°C, with temperatures greater than 1200°C being optimal.

The high deposition temperatures associated with these CVD processes often promote the decomposition and/or reaction of the substrate. This can

Mat. Res. Soc. Symp. Proc. Vol. 131. ©1989 Materials Research Society

lead to the deposition of films that are neither phase nor compositionally homogeneous and pure. In addition, film microstructure, composition, and adherence are adversely effected by the corrosive gaseous by-products of these processes [6]. Finally, control of the microstructure, thickness, and purity of the films is limited in lower temperature CVD processes. Carrying out these CVD processes at lower total pressures, 1-100 torr, can improve control over these properties; however, the associated deposition temperatures of greater than 1200°C limit the choice of potential substrates [7].

To circumvent these difficulties, we have investigated the synthesis and low pressure chemical vapor deposition (LPCVD) of volatile, heterocyclic, organometallic precursors. Previously, we reported the CVD of SiC using a cyclic carbosilane precursor, $[MeHSiCH_2]_3$ [8]. More detailed studies have shown that the compound employed was actually a four-membered ring carbosilane, $MeHSi\overline{CH_2SiCH_2}Me(CH_2SiMeH_2)$, a structural isomer of the expected six-membered ring compound. The research described herein provides additional information on the preparation and characterization of SiC films obtained from LPCVD studies employing this precursor at substrate temperatures between 600 and 900°C.

EXPERIMENTAL

Synthesis and Characterization of $Me(H)SiCH_2SiCH_2Me(CH_2SiMeH_2)$.

The preparation of the cyclic carbosilane was based on the Grignard coupling reactions discussed by Kriner, as summarized in equation 1 [9]. Spinning band distillation of the pale yellow liquid product of the reduction

$$MeSi(Cl_2)CH_2Cl + Mg \longrightarrow \underset{\text{and other prods.}}{[MeSi(Cl)CH_2]_n} \xrightarrow{LiAlH_4} \underset{\text{and other prods.}}{[MeSi(H)CH_2]_n} \qquad (1)$$

with $LiAlH_4$ yielded a colorless liquid, b.p.=73-75°C at 33 torr, in *ca.* 15% overall yield. The gas chromatogram of this liquid showed two peaks indicating a mixture of 85% of the cyclic carbosilane, $MeHSi\overline{CH_2SiCH_2}Me(CH_2SiMeH_2)$, and 15% of an impurity which was tentatively identified as $Me_2Si(CH_2SiH_2Me)_2$. Samples for analytical studies were collected directly from the GC; whereas the mixture was used in the CVD experiments. Subsequent analysis of the major component of this liquid fraction by ^1H and ^{29}Si NMR indicated that it was comprised of an approximately 50/50 mixture of the expected *cis* and *trans* geometric isomers of the cyclic carbosilane.

Mass spectrometric analysis: m/e 174 (M^{+1}), 173, 159, 129, 115, 99, 85, 73, and 59. IR: 2960 (s), 2900 (m), 2870 (w), 2120 (vs), 1400 (w), 1340 (m), 1245 (s), 1040 (vs), 940 (vs), 900 (vs), 800 (vs), 750 (m) and 700 (m) cm^{-1}. ^1H NMR: -0.15 (two triplets), -0.01 (multiplet), 0.07 (two triplets), 0.14 (multiplet), 0.25 (2 doublets, 2 singlets), 0.4 (multiplet), 4.1 (2 sextets), and 4.9 (multiplet) ppm. $^{29}Si\{^1H$ coupled$\}$: -39.1 (triplet), -15 (doublet), 7.5 (singlet), and 8.5 (singlet) ppm.

Apparatus and Procedure for the CVD of SiC from $MeHSiCH_2SiCH_2Me(CH_2SiCH_2Me)$

Details of the substrate preparation, horizontal, hot-wall CVD reactor, and analytical instrumentation are presented elsewhere [10]. In typical experiments, *ca.* 0.5-1.0 g of the carbosilane precursor was loaded into the precursor container fitted with a high vacuum greaseless stopcock and o-ring joint, in an N_2 filled glove box. After connecting the precursor container to the reactor and evacuating the system to 10^{-5} torr, the substrates (cleaned Si(111) or (100) wafer pieces and silica plates) were heated to 800°C for several hours. The furnace was set to the deposition temperature, between 600 and 900°C, the precursor frozen with liquid nitrogen, and the precursor container opened to the reactor and vacuum system. Subsequently, the precursor was warmed to 0-20°C and vaporized into the reactor using a mechanical/diffusion pump system. The typical steady-state pressure of the CVD reactor was 0.5-0.9 torr. After deposition, the reactor was cooled to room temperature and opened to air.

Gas phase pyrolysis products of the precursor were analyzed by gas chromatography, FTIR, and NMR. The thin films were examined by SEM, Auger spectroscopy, electronic absorption and FTIR spectroscopy, ellipsometry, and XRD measurements.

The adsorption behavior and decomposition of the carbosilane precursor on a clean Si(100) surface were studied in an ultra- high vacuum apparatus, containing a sample holder/positioner, a quadrupole mass spectrometer and a cylindrical mirror based system for Auger electron spectroscopy [11]. The precursor (equilibrium vapor pressure *ca.* 2 torr at room temperature) was admitted through a solenoid operated pulsed valve.

RESULTS AND DISCUSSION

Chemical Vapor Deposition of SiC Films in the Hot-Wall Reactor

Pure, dense, polycrystalline SiC films were deposited on silicon and fused silica substrates by the thermal decomposition of $MeHSiCH_2SiCH_2Me(CH_2SiMeH_2)$ at temperatures of 700-900°C and pressures of 0.5-0.9 torr. Film thicknesses ranged from a few hundred Angstroms to one micron, depending on the time, quantity of precursor employed, and the substrate and precursor temperatures. The deposition rates were typically 100-150 A/min.

The surface morphology of the SiC films was studied by SEM and optical microscopy. Optical micrographs of the pale yellow, transparent films indicated a smooth, uniform, and featureless surface. Scanning electron micrographs of these SiC films showed a uniform, non-porous, and fine-grained surface. The scanning electron micrographs of SiC film cross-sections illustrate that the films are adherent to the substrate, with no indication of crystalline orientation or porosity. A representative scanning electron micrograph of an SiC film deposited on a Si(111) surface at 800°C is shown in Figure 1. X-ray powder diffraction studies indicate that these films are noncrystalline or nanocrystalline. TEM and selected area diffraction analyses to obtain additional information on film microstructure are in progress.

Compositional analyses of the SiC films prepared at 700-800°C by Auger electron spectroscopy indicated that the films were essentially stoichiometric, % Si=49 and % C=51, with oxygen levels in the bulk of less than 0.8%. These results were derived by comparison to measurements made on a single crystal of 6H-SiC of known 1:1 stoichiometry. A representative

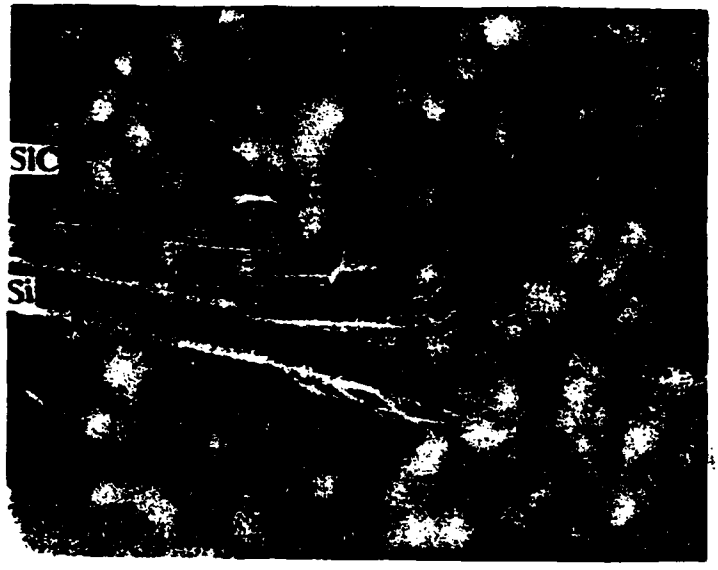

Figure 1. SEM of a SiC-coated Si wafer piece broken to reveal the SiC layer.

Auger depth profile of an SiC film deposited on Si(111) substrate at 800°C is shown in Figure 2. The FTIR transmission spectrum of this film showed a single strong band at *ca.* 800 cm^{-1}, as expected for SiC. Optical absorption studies carried out on a *ca.* 0.5 μm, pale-yellow, transparent film deposited on SiO_2 at 800 °C showed no absorbance from 900 to 550 nm with a gradually accelerating increase in absorbance at lower wavelengths to a cut-off at around 300 nm.

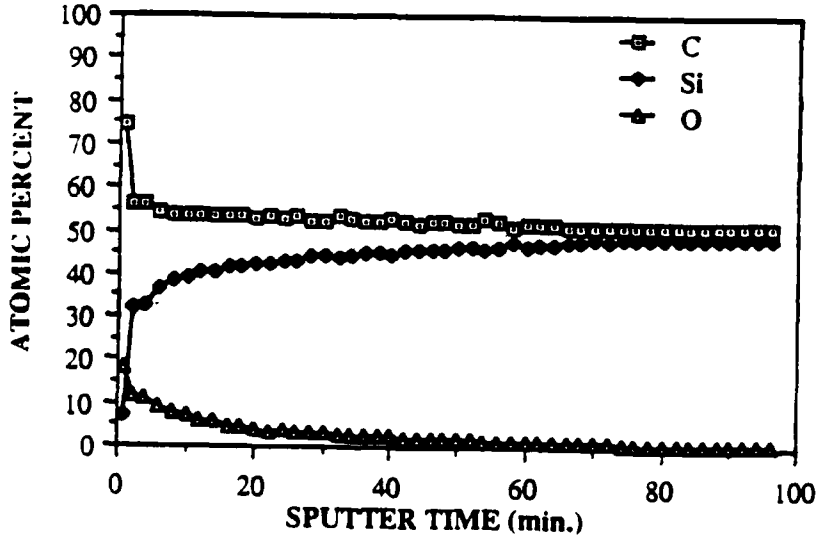

Figure 2. Auger depth profile of an 800 °C SiC film on Si.

At a deposition temperature of 600°C, no SiC was deposited, with most of the carbosilane precursor passing through the reactor and collecting in the liquid nitrogen-cooled trap. Films deposited at 900°C contained higher proportions of carbon than 1:1 and were black and shiny in appearance. Auger depth profiles on two such films showed Si:C ratios of 1:1.46 and 1:1.75. The oxygen content of these films was less than 0.8%.

Measurements of the refractive index, using an ellipsometer with a 70° incident light angle and a wavelength of 6328 A, gave a value (2.7±0.1) which was very close to that of single crystal SiC [12] for the films deposited at 700-800 °C. The refractive index values obtained for the carbon-rich SiC films deposited at 900 °C were considerably higher (3.0±0.1), possibly due to the non-stoichiometry and multiple scattering from SiC_{1+x} or C particles.

Preliminary investigations of the gas phase pyrolysis products of the CVD processes were carried out by collecting the gases in the liquid nitrogen trap and separating them by gas chromatography. In a separate experiment the precursor was swept with nitrogen past a SiO_2 probe, heated to *ca.* 800 °C with a nichrome heating element, and the gas mixture was analyzed downstream by GC. The latter analyses indicated the presence of H_2 and methane, with a small amount of other hydrocarbons. The gaseous products obtained on warming the contents of the liquid nitrogen trap to room temperature were mainly ethylene and acetylene, with small amounts of methane and ethane. In addition, a small amount of a liquid byproduct was obtained which ^1H NMR studies suggest contain one or more silane compounds in addition to unreacted precursor. More detailed analyses of the gas and liquid by-products of the CVD processes are in progress; however, it is apparent that the pyrolysis chemistry is quite complex, probably involving homolysis of the CH_3, H, and $CH_2SiH_2CH_3$ groups on the cyclic carbosilane as radical species, followed by subsequent radical coupling and H-abstraction to give the various hydrocarbon and silane byproducts observed.

Precursor Interactions with Si(100) in the Ultrahigh Vacuum System

Measurements were first made at low temperature to characterize the adsorption behavior of the intact precursor. While cooling the sample to 130K the pulse valve was operated for 100 to 5000 pulses to deposit the precursor on the Si(100) surface. The sample was then heated at a linear rate of 4.6K/sec and one of the precursor mass peaks (mass 73) monitored with the mass spectrometer. Two approximately equal area desorption peaks were observed in all cases, presumably corresponding to the two geometrical isomers of the cyclic carbosilane. In a second set of measurements the pulse valve was operated while the substrate temperature was increased in increments above room temperature, and the resulting waveform of signal vs time on the detector mass spectrometer, tuned to mass 73, was collected. For temperatures above about 400K, all waveforms had essentially the same shape, approximating that of the pulse valve, convoluted with the pumping time constant of the main chamber. As the substrate was heated beyond about 800K the amplitude of the waveform was attenuated signaling the onset of decomposition of the precursor on the surface. Attempts to detect waveforms of the expected gas-phase product species, such as CH_3, CH_4, C_2H_6, and H_2 were made; however, no signal coherent with the pulsing process was observed at any of these masses.

Auger spectra taken before exposure to the precursor species showed only peaks attributable to silicon. After exposure to precursor at temperatures above 800K, a carbon peak was also visible with a carbon-to-silicon ratio

consistent with the formation of a SiC layer on the surface.

At the conclusion of these studies, the samples were further investigated by scanning electron microscopy and transmission electron microscopy. Small etch features (pits) were observed by SEM in the area of the sample that had been exposed to the precursor beam. Overlying part of these etched areas and the intervening region between them was a smooth, continuous film. This observation, coupled with the failure to observe any hydrocarbon by-products during the CVD reaction, suggests that the Si(100) substrate is reacting, presumably with the carbon-containing byproducts, to form SiC in this low coverage regime. The absence of such etch pits in the case of the samples obtained from the hot-wall reactor suggests further that the surface and/or gas phase chemistry may be fundamentally different in these two systems.

One sample from the ultra-high vacuum studies was thinned electrochemically and examined in the transmission electron microscope. An image of the film is shown in Figure 3. Selected area diffraction measurements taken on this same area, shown in the inset to Figure 3, gave a pattern consistent with a fine-grained, polycrystalline silicon carbide. Because of the small differences among the various SiC polytypes, unequivocal identification of the phase(s) present was not possible; however, it was apparent that there was some preferred orientation in the SiC, with <111> SiC || <111> Si. While there is not complete epitaxial growth of SiC, it is significant that as-deposited some degree of lattice matching is occurring at the interfaces.

Figure 3. Transmission electron micrograph of a SiC film deposited on Si(100). The diffraction pattern of a selected area of this film is shown in the inset.

ACKNOWLEDGEMENTS

We thank Mr. Chris Whitmarsh for synthesizing the carbosilane precursor and Mr. Ray Dove and Dr. Krisna Rajan for assistance with the SEM and TEM analyses. This work was supported by the Office of Naval Research under Contract No. N0001485K0632.

REFERENCES

1. Schlichting, J. *Powder Met. Intl.* **12**, 141 (1980).
2. Lely, A. *Ber. Dtsch. Keram. Ges.* **32**, 229 (1955).
3. O'Connor, J.R.; Smiltens, J., eds. Silicon Carbide, A High Temperature Semiconductor. New York: Permagon Press (1960).
4. Marshall, R.; Faust, J.; Ryan, C., eds. Silicon Carbide-1973. Columbia, S.C.: University of South Carolina Press (1974).
5. Campbell, R.B.; *IEEE Trans. Indus. Electr.*, **IE-29**, 124 (1980).
6. Bessman, T.M.; Stinton, D.P; Lowden, R.A.; *MRS Bull.* 45 (1988).
7. Fujiwara, Y.; Sakuma, E.; Misawa, S.; Endo, K.; Yoshida, S. *Appl. Phys. Lett.* **49**, 388 (1986).
8. Interrante, L.V.; Czekaj, C.L.; Lee, W. *NATO Meeting Proc.-The Mechanisms of Reaction of Organometallic Compounds with Surfaces*. London: Plenum Press (1988), in press.
9. Kriner, W. *J. Org. Chem.* **29**, 1601 (1961).
10. Interrante, L.V.; Lee, W.; McConnell, M; Lewis, N.; Hall, E. *J. Electrochem Soc.* in press.
11. Kurtz, E.A.; Hudson, J. *Surface Sci.*, **195**, 15 (1988).
12. Palik, E.D., ed. Handbook of Optical Constants of Solids. New York: Academic Press (1985), p 587.